

Ewa M. SERWICKA¹, Krzysztof BAHRANOWSKI², Roman DULA¹,
Adam GAWĘŁ², Alicja MICHALIK², Paweł NOWAK¹

SYNTHESIS OF HYDROTALCITE-LIKE ANIONIC CLAYS PILLARED WITH KEGGIN-TYPE HETEROPOLYMOLYBDATES

Abstract. A series of hydrotalcite-like anionic clays intercalated with the Keggin-type $(PV_nMo_{12-n}O_{40})^{(3+n)-}$ heteropolyanions have been synthesized by means of anion exchange and characterized with XRD, IR and BET techniques. The results show that the intercalation is complete and yields a phase with a d spacing of 14.6 Å corresponding to Keggin anion pillared clay (minor product), and a phase with a less-defined interlayer distance of ca. 11–12 Å (major product). The latter value of d spacing is connected either with the occurrence of defect layers resulting from partial local dissolution of brucite sheets due to the interaction with acidic heteropolyanions, or to the presence of lacunary Keggin species of smaller dimensions. The formation of the phase with large d spacing is enhanced upon intercalation of anions with a high negative charge. A new way of adapting the charge on the anion to the requirements of the intercalation procedure, by means of electrochemical reduction, has been proposed and tested on 12-molybdophosphate anion. XRD shows that the anion with the charge reduced by 4 electrons is more suitable for intercalation than the non-reduced species.

Key-words: hydrotalcite, pillared clays, anionic clay.

INTRODUCTION

The term 'anionic clay' is used to designate the family of lamellar ionic solids, natural or synthetic, built of positively charged hydroxide layers whose charge is compensated by anionic species present in the interlayer (Cavani et al. 1991). They are also known under the name of 'layered double hydroxides', which reflects the presence of two kinds of cations in the sheets of these compounds. Hydrotalcite-like compounds are synthetic phases isomorphous with the natural hydrotalcite which is an anionic clay mineral of the formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. Their general formula is $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{m-}_{x/m} \cdot nH_2O]$, where M^{II} and M^{III} are

¹ Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 1, 30-239 Cracow, Poland.

² Faculty of Geology, Geophysics and Environmental Protection, University of Mining and Metallurgy, Mickiewicza 30, 30-059 Cracow, Poland.

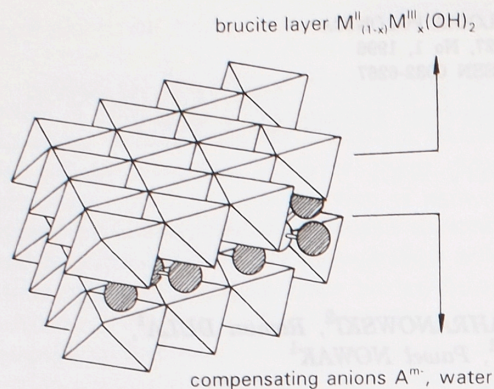


Fig. 1. Schematic illustration of a hydrotalcite-like structure

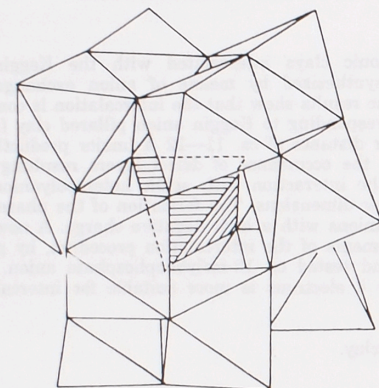


Fig. 2. Structure of the Keggin anion

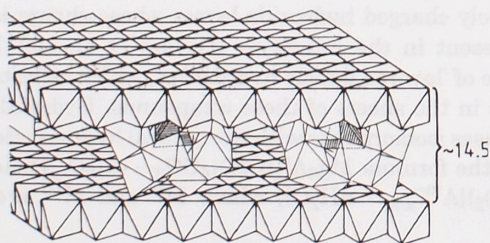


Fig. 3. Schematic illustration of a hydrotalcite clay intercalated with Keggin anions

the cations in the hydroxide layers and A^{m-} is the interlayer anion (Fig. 1). A very large range of compositions with different M^{II} , M^{III} and A^{m-} can be prepared (Cavani et al. 1991). Intercalation of bulky heteropolyoxometalate species represents a particular challenge, as the materials obtained in such a way may be of potential importance in catalysis. Depending on the number of condensing metal cations and heteroatoms, discussed the heteropolyoxometalates may adopt different structures (Pope 1984). One of the most studied is the so-called Keggin-type structure (Fig. 2), where 12 metal-oxygen octahedra form a shell surrounding tetrahedrally coordinated heteroatom. The dimension of a Keggin heteropolyanion is around 10 Å, therefore its insertion between the hydroxide sheets should induce a significant expansion of the crystal lattice (Fig. 3). This is not an easy task, first, because the charge density in hydrotalcite-like compounds is rather large (ca. 0.04 electron/Å² for $M^{II}_{0.67}M^{III}_{0.33}$ composition, in comparison with ca. 0.01 electron/Å² in montmorillonite), and the electrostatic forces holding the layers together are quite strong, and second, because the heteropolyanions stability requires acidic medium which may bring about a partial dissolution of hydrotalcite matrix. The first information on the possibility of synthesis of heteropolyoxometalate-hydrotalcite-like intercalates

stems from the patent by Woltermann (1984), but first paper describing the synthesis and providing physicochemical characterization of the product was published by Kwon and Pinnavaia only in 1989. There, the authors concluded that for a successful intercalation of a Keggin-type anion in a hydrotalcite-like compound, the heteropoly species should carry possibly large charge, in order to be able to compensate the excess positive charge of the hydroxide layer. Assuming the dense packing of heteropolyanions, it can be calculated that the minimum negative charge on a heteropolyanion intercalated into a hydrotalcite of the above composition should be at least 4. Various means supposed to facilitate this task have been proposed, such as the use of an organic anion pillar as an intermediate, accompanied by the use of glycerol as a swelling agent (Dimotakis and Pinnavaia 1990) or thorough soaking of the hydrotalcite material in water before the intercalation experiment (Wang et al. 1992). In the majority of intercalation experiments reported up to now, mainly heteropolytungstate anions have been investigated (Kwon and Pinnavaia 1989; Dimotakis and Pinnavaia 1990; Narita et al. 1991; Wang et al. 1992; Zheng and Yue 1994; Hu et al. 1996). However, of particular interest from the point of view of potential application in catalysis would be an intercalation of such species as 12-molybdophosphate anions pure, and partially substituted with vanadium $(PV_nMo_{12-n}O_{40})^{(3+n)-}$. These compounds are known to possess very strong redox properties and are powerful redox catalysts (Pope, 1984; Serwicka et al. 1987).

The aim of the present work was twofold: a) to check on the possibility of intercalation of heteropolyanions belonging to the $(PV_nMo_{12-n}O_{40})^{(3+n)-}$ ($n = 0, 1, 2$) series into the hydrotalcite-like synthetic compound, and b) to find means to increase the net charge on a heteropolyanion so as to increase its ability of balancing the layer charge in hydrotalcite-like compounds. To realize the latter goal we resorted to electrochemical reduction of heteropolyanions. It is known that heteropolyanions undergo facile reduction by several electrons per Keggin unit, to give so-called heteropoly-blues (Pope, 1984). We used this capability to increase the negative charge on the $PMo_{12}O_{40}^{3-}$ anion and in such a way produce species better able to compensate the positive layer charge of the hydrotalcite matrix.

EXPERIMENTAL

Synthesis details

Analytical-grade reagents were used for all preparations described in this work. Anionic exchange was used for intercalation of heteropolyanions into the parent hydrotalcite-like compound.

Starting hydrotalcite-like compounds:

a) $[Mg_{0.67}Al_{0.33}(OH)_2](NO_3)_{0.33}$

A solution containing 0.12 M $Mg(NO_3)_2$ and 0.06 M $Al(NO_3)_3$ dissolved in 50 ml

water was added dropwise to 100 ml of NaOH solution at pH = 10. The experiment was performed under nitrogen atmosphere to avoid contamination with carbon dioxide, which in aqueous medium easily reacts with hydrotalcite matrix. The resulting white slurry was heated at 328 K for 24 h, washed with distilled water and dried in air at 333 K. The sample is further referred to as MgAlNO_3 .

Preparation of hydrotalcites intercalated with $(\text{PV}_n\text{Mo}_{12-n}\text{O}_{40})^{(3+n)-}$ anions:

0.5 g of parent hydrotalcite was added to 50 ml of water solution containing 0.5 mmol of heteropolyanion $(\text{PV}_n\text{Mo}_{12-n}\text{O}_{40})^{(3+n)-}$ ($n = 0, 1, 2$) obtained according to the method described by Tsigdinos (1974). The mixture was left at room temperature for 2–18 h under continuous stirring. The final pH was ca. 4.0–4.5. The resulting solid was filtered, washed with distilled water, and dried at room temperature. The samples are further referred to as $\text{MgAlPV}_n\text{Mo}_{12-n}$.

Preparation of hydrotalcites intercalated with reduced $(\text{PMo}_{12}\text{O}_{40})^{7-}$ anion:

15 g of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 30\text{H}_2\text{O}$ (ca. 7 mmol) was dissolved in 66 ml water and reduced in an electrochemical cell to a degree corresponding to the transfer of 4 electrons per each Keggin unit. The resulting reduced anion, characterized by a deep blue colour, can be thus described as $\text{PMo}_{12}\text{O}_{40}^{7-}$. 0.5 g of the parent MgAlNO_3 was added to 5 ml of the blue solution diluted to 50 ml with distilled water. The mixture was stirred for 2 h at room temperature. The final pH was 4.0. The resulting blue solid was filtered, washed with distilled water, and dried at room temperature. The sample is further referred to as $\text{MgAlPMo}_{12}(\text{red})$.

Physicochemical characterization

X-ray diffraction analysis

XRD patterns were obtained with a DRON-3 diffractometer using Ni-filtered CuK_α radiation.

Infrared spectroscopy

IR spectra were recorded with a Nicolet 800 FTIR spectrometer.

BET measurement

The BET surface area of the samples was determined from argon adsorption at 77 K, after outgassing at 473 K for 2 h.

RESULTS AND DISCUSSION

The main technique providing information whether the intercalation procedure was successful is X-ray diffraction. Assuming the layer thickness of ca. 4.4 Å and the Keggin ion diameter of 9.8 Å, the basal spacing after intercalation should be at least 14.2 Å. Fig. 4a shows X-ray diffraction recorded for the parent MgAlNO_3 compound. The 00 l harmonics of the basal spacing, i.e. 8.87 Å and 4.42 Å, are marked. The examples of X-ray powder patterns obtained for heteropolyanion-ex-

changed samples are presented in Fig. 4b–e. It may be seen that in the course of intercalation the basal spacing characteristic of the parent compound disappears. Instead, in the intercalated samples new reflections appear, but only in Fig. 4c–e patterns expected for the intercalation product can be detected. In Fig. 4c, for the MgAlPVMo_{11} sample, a shoulder corresponding to ca. 14.3 Å can be seen, in Fig. 4d, for the $\text{MgAlPV}_2\text{Mo}_{10}$ sample, apart of the basal spacing of 14.6 Å also higher order reflexes of 7.31 Å, 4.84 Å and 3.62 Å appear, and in Fig. 4e, showing the XRD powder pattern of hydrotalcite intercalated with the electrochemically reduced species $\text{MgAlPMo}_{12}(\text{red})$ also a low angle reflex of 14.7 Å appears, followed by 7.38 Å and 4.90 Å harmonics. However, apart of the patterns expected for the hydrotalcites intercalated with Keggin anions, which are clearly the minor products, other reflections appear, dominated by a broad peak around 11–12 Å, and obviously associated with the major product. This type of XRD patterns is usual for hydrotalcites intercalated with heteropolyoxometalates (Narita et al. 1991; Wang et al. 1992; Zheng and Yue 1994). Wang et al. (1992) assigned the appearance of pillared products with smaller than expected d

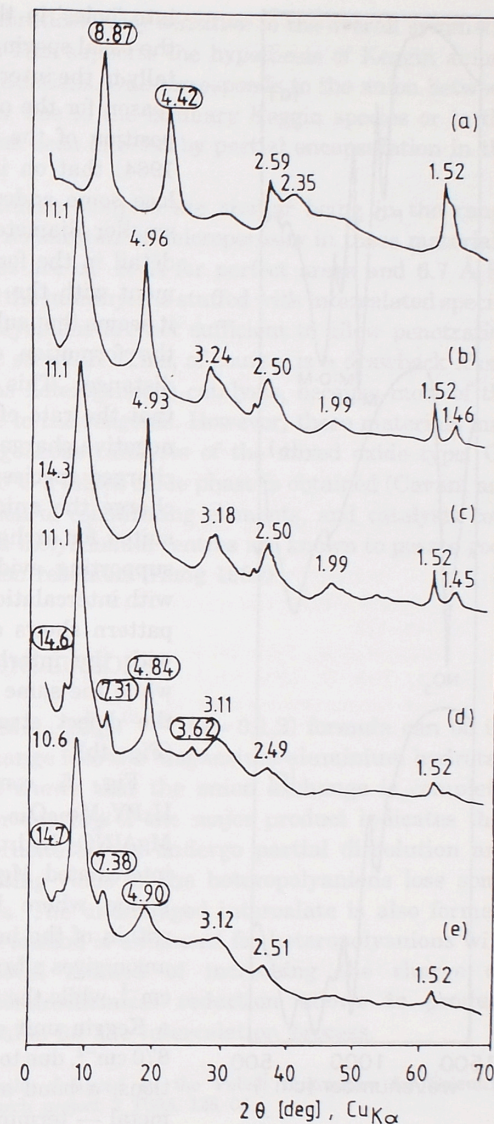


Fig. 4. XRD powder patterns of a) MgAlNO_3 , b) MgAlPMo_{12} , c) MgAlPVMo_{11} , d) $\text{MgAlPV}_2\text{Mo}_{10}$, e) $\text{MgAlPMo}_{12}(\text{red})$

spacings to interactions between the essentially basic hydrotalcite matrix and the acidic Keggin anions. The acidic medium create structural defects in the layers by partial local dissolution of the brucite sheets. Fitting of the Keggin anions

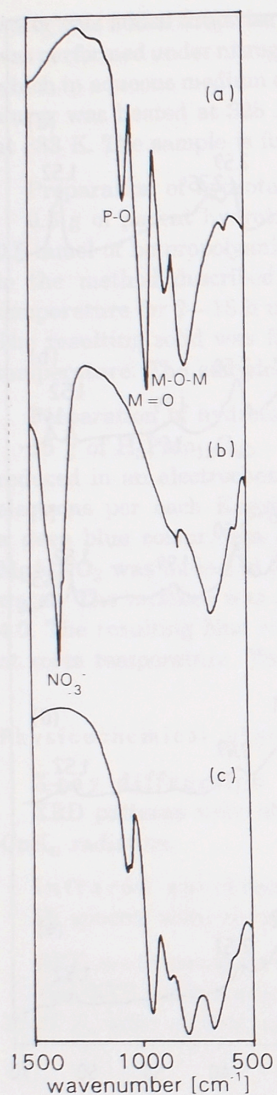


Fig. 5. FTIR spectra of a) $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, b) MgAlNO_3 , c) $\text{MgAlPV}_2\text{Mo}_{10}$.

before and after intercalation with the heteropolyanion is the disappearance of the band at ca. 1380 cm^{-1} , characteristic of NO_3^- ions, and the appearance of the bands typical of the Keggin unit. This confirms that anion exchange is complete and the heteropolyanion replaced the nitrate anion in the structure of hydrotalcite. However,

into 'holes' in the hydroxide layers would lead to the basal spacing in the range observed experimentally in the intercalation products. Another possible reason for the observed d values is partial decomposition of the Keggin anion. It is known (Pope 1984) that on increasing pH Keggin anions may lose some addenda and form lacunary species of smaller diameter. We shall discuss this point in detail in the forthcoming paper. From our experiment with the series of $(\text{PV}_n\text{Mo}_{12-n}\text{O}_{40})^{(3+n)-}$ ions it seems that substitution with vanadium enhances the formation of product with larger interlayer distances. This is most probably due to the fact that the rate of incorporation of anion with large negative charge is higher than in the case of less charged species. Also, on increase of the negative charge the anions become less acidic and better suited for exchange reaction with hydrotalcites. A supporting evidence comes from the experiment with intercalation of reduced $\text{PMo}_{12}\text{O}_{40}^{7-}$. The XRD pattern shows clearly the appearance of a phase with the interlayer spacing of 14.7 \AA (Fig. 4e), while the same anion before reduction shows only the defect structure with d spacing of 11.1 \AA (Fig. 4b).

Fig. 5 compares the IR spectra of the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ heteropolyacid (Fig. 5a), the initial MgAlNO_3 hydrotalcite compound (Fig. 5b) and the intercalated $\text{MgAlPV}_2\text{Mo}_{10}$ sample (Fig. 5c) in the region where bands characteristic of vibrations within of the intercalated anions appear. The NO_3^- anion gives a broad band with maximum at ca. 1380 cm^{-1} , while the very characteristic pattern typical of a Keggin unit consists of bands around 780 cm^{-1} , 870 cm^{-1} , due to the metal — bridging oxygens vibrations, a band at ca. 960 cm^{-1} associated with the metal — terminal oxygen vibrations and a band at 1060 cm^{-1} connected with heteroatom-oxygen vibrations (Alpert et al. 1970). It may be seen that the major change in the IR spectrum of the hydrotalcite

the band characteristic of the P-O vibrations, very sensitive to the overall symmetry of the anion, shows a distinct split. This supports the hypothesis of Keggin anions present in two different structural situations. One corresponds to the anion between the intact layers, the other is either due to the lacunary Keggin species or to the heteropolyanion whose symmetry has been affected by partial encapsulation in the faulty areas of brucite sheets.

BET surface areas of all hydrotalcite samples are similar being in the range $20\text{--}40\text{ m}^2/\text{g}$. It means that there is no substantial microporosity in these materials, even though the interlayer distances are ca. 10 \AA for perfect areas and 6.7 \AA for defect structures. This indicates that the interlayer is stuffed with intercalated species and distances between the heteropolyanions are not sufficient to allow penetration of argon atoms into the hydrotalcite structure. This, of course, is a drawback if one would like to use these materials as heterogeneous catalysts, because most of the active phase would not be accessible to the reagents. However, these materials may be very good precursors for heterogeneous catalysts of the mixed oxide type. On calcination at temperature above 500°C a mixed oxide phase is obtained (Cavani and Trifiro 1991) with unique distribution of constituting elements, and catalysts containing well dispersed vanadium and molybdenum centres are known to possess good activity in catalytic selective oxidation reactions (Kung 1989).

CONCLUSIONS

Phosphomolybdates of the $(\text{PV}_n\text{Mo}_{12-n}\text{O}_{40})^{(3+n)-}$ ($n = 0, 1, 2$) formula can be intercalated by means of anionic exchange into the magnesium-aluminium hydrotalcite-like compound. IR experiment shows that the anion exchange is complete. The lower than expected interlayer spacing of the major product indicates that either upon intercalation of the brucite layers undergo partial dissolution and the Keggin anions enter the resulting voids or the heteropolyanions lose some addenda and form lacunary species. The undamaged intercalate is also formed, although as a minor product. Its formation is enhanced for heteropolyanions with a higher negative charge. A novel method of increasing the charge on heteropolyanions by means of electrochemical reduction allows to produce heteropolyanion species better suitable for the intercalation process.

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SYNTEZA MINERAŁÓW TYPU HYDROTALKITU PODPIERANYCH HETEROPOLIMOLIBDENIANAMI O STRUKTURZE KEGGINA

Streszczenie

Stosując wymianę jonową otrzymano serię syntetycznych minerałów typu hydrotalkitu interkalowanych heteropolianionami typu Keggina o wzorze $(\text{PV}_n\text{Mo}_{12-n}\text{O}_{40})^{(3+n)-}$ ($n = 0, 1, 2$). Produkty syntezy zostały scharakteryzowane metodami analizy rentgenowskiej, spektroskopii IR oraz BET. Wyniki wskazują, że wymiana anionów jest całkowita, a w produktach reakcji obserwuje się fazę mniejszościową

o odległościach międzywarstwowych $14,7 \text{ \AA}$, odpowiadającą oczekiwanej strukturze hydrotalkitu podpieranego anionami Keggina, oraz fazę większościową charakteryzującą się gorzej zdefiniowaną odległością międzywarstwową rzędu 11 \AA . Może ona być produktem interkalacji heteropolianionów w obrębie silnie zdeformowanych warstw hydrotalkitu powstałych na skutek częściowego rozpuszczania zasadowej warstwy brucytowej w kwaśnym środowisku heteropolianionów lub też powstawać jako efekt interkalacji częściowo zdysocjowanych anionów Keggina. Tworzeniu fazy o dużej odległości międzywarstwowej sprzyja możliwie wysoki ładunek interkalowanego anionu. Zaproponowano nową metodę dopasowywania ładunku anionu do potrzeb interkalacji przez zastosowanie elektrochemicznej redukcji heteropolianionów i wypróbowano ją na przykładzie jonu 12-molibdenofosforowego. Analiza rentgenowska wykazała, że anion zredukowany 4 dodatkowymi elektronami lepiej nadaje się do interkalacji niż forma niezredukowana.